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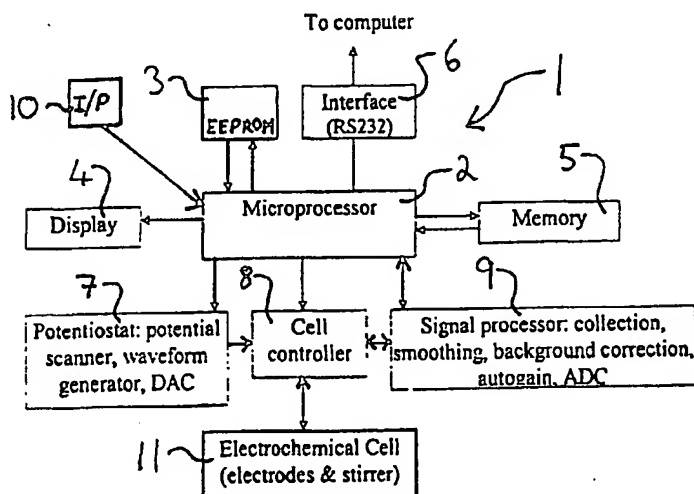
(57) Abstract

Apparatus (1) for voltammetric analysis includes a processor (2) and a first memory device (3) coupled to the processor (2). The first memory device (3) comprises a programmable read only memory and stores a number of electrochemical cell control programs. An output device (4), an input device (10), a second memory device (5) and an electrochemical cell controller (7, 8, 9) are also coupled to the processor (2). The cell controller (7, 8, 9) is adapted to be coupled to an electrochemical cell (11). The processor (2), in response to an analyte input signal entered via the input device (10), retrieves a corresponding electrochemical cell control program, and instructs the cell controller (7, 8, 9) to apply a scanning voltage to the electrochemical cell (11), in accordance with the retrieved control program. The processor (2) also processes output signals received by the cell controller (7, 8, 9) from the electrochemical cell (11), in response to the applied scanning voltage, to obtain an indication of the concentration of an analyte, corresponding to the analyte input signal, in the electrochemical cell (11), and outputs the indication to the output device (4).

APPARATUS FOR VOLTAMMETRIC ANALYSIS

The invention relates to apparatus for voltammetric analysis.

Voltammetric analysis is a widely used electroanalytical
technique. The art of this technique has been well described
in many publications [1,2]. Voltammetric analysis can be
carried out using various waveforms, for example, linear,
pulse, square and AC or using various operation modes, for
example cyclic voltammetry and stripping voltammetry [3].
Many inventors have disclosed specific devices and methods for
voltammetric analysis. Girault [4] showed a device for change
of electrodes. Fidler *et al* [5] disclosed a circuit to
maintain a stable potential difference between the working and
the reference electrodes. Tur Yan *et al* [6] used a special
cell to detect trace metals using stripping voltammetry.
Saloheimo *et al* [7] introduced ultrasonic vibration during
pre-electrolysis in stripping voltammetry. Other researchers
have designed special electrodes for anodic stripping
voltammetry [8-10].

Kissinger [11] predicted the future of electroanalytical
instrumentation as being computerization, miniaturization and
automation. Computers have been used to collect
electrochemical signals [12], to acquire data and control
experiments [13] and to modify waveforms [14]. Computerised
voltammetric instruments are now commercially available from
many instrument manufacturers.

However, computerised voltammetric instruments are generally
large in size and costly. Small polarographic or voltammetric
analysers are available for specific analytes, such as
aldehyde [15] and lead [16]. Multi-element analysis using
this type of equipment can be achieved by using multichannel
selection [17] or multi-electrodes [18]. However, the number
of elements that can be analysed is physically limited.

In addition, the process of voltammetric analysis often
involves many decision making steps. Although computerised
voltammeters can run analysis automatically it is still
necessary for the supporting electrolytes, calibration
standards and experimental conditions, such as initial
potential, final potential, scan rate and current range, to be
chosen by an operator before the analysis commences. During
analysis, voltammograms with peak currents or peak areas need
to be acquired, and after analysis, the data requires
processing and the results reported. These decision making
steps require trained personnel with knowledge and experience.
Although they can be simplified into a computer program as
demonstrated by De kreuk *et al* [19] in an automatic stripping
voltammetric method, as indicated by some researchers [20],
automation of voltammetric instrument is a more complicated
task than that of other electroanalytical techniques. Hence,
automation is often at the level of operation rather than the
decision making process.

Therefore, even computerised and highly automated systems

still require skilled and experienced personnel to operate
them.

In addition, conventional electrodes for voltammetry have the
problem that it is difficult to ensure good electrical contact
between the electrode and the electrical wire coupling the
electrode to the analysing equipment. In particular, with
some types of electrode, such as glassy carbon, it is not
possible to solder the electrical wire to the electrode.
Accordingly, conventional methods of electrically contacting
the wire to the electrode include using mercury to bond the
wire to the electrode or using conductive glue. Mercury has
the disadvantage that it is toxic and the conductive glue has
the disadvantage that it is not easy to disconnect the
conductor from the electrodes.

In accordance with a first aspect of the present invention,
apparatus for voltammetric analysis comprises a processor; a
first memory device coupled to the processor, the first memory
device comprising a programmable read only memory and storing
a number of electrochemical cell control programs; an output
device coupled to the processor; an input device coupled to
the processor; a second memory device coupled to the
processor; an electrochemical cell controller coupled to the
processor, the cell controller being adapted to be coupled to
an electrochemical cell; the processing device, in response to
an analyte input signal entered via the input device,
retrieving a corresponding electrochemical cell control

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program, and instructing the cell controller to apply a
scanning voltage to an electrochemical cell coupled to the
cell controller in use, in accordance with the retrieved
control program, and processing output signals received by the
cell controller from the electrochemical cell, in response to
the applied scanning voltage, to obtain an indication of the
concentration of an analyte, corresponding to the analyte
input signal, in the electrochemical cell, and outputting the
indication to the output device.

Preferably, the programmable read only memory is an
electrically erasable programmable read only memory (EEPROM).

Preferably, the output device comprises a display device, such
as a liquid crystal display (LCD). However, alternatively or
in addition, the output device may comprise an interface
device which permits the processor to communicate with another
processing device, such as a computer, or with a storage
device, such as a magnetic disk or tape drive.

Preferably, the cell controller includes a potentiostat and a
signal processor.

Preferably, the apparatus is for stripping voltammetric
analysis of an analyte in an electrochemical cell.

In accordance with a second aspect of the present invention,
an electrochemical cell comprises a container comprising a

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bottom portion, an upper portion and an opening to permit a liquid to be analysed to be introduced into the container; a stirring device depending from the upper portion into the bottom portion of the container; and a counter electrode and a working electrode depending from the upper portion into the bottom portion of the container.

Preferably, the axis of rotation of the stirring device is substantially co-axial with the central vertical axis of the container and the counter and working electrodes are arranged around the stirring device.

Typically, the upper portion of the container, may be separated from the bottom portion of the container to permit liquid to be inserted into the container prior to engagement of the upper portion with the bottom portion.

Typically, the bottom portion may be in the form of a jar or other liquid containing device and the upper portion may form a lid for the jar or containing device.

Preferably, the electrochemical cell further comprises a reference electrode which also depends from the upper portion of the container such that the reference electrode is adjacent the stirring device and located between the counter and the working electrodes.

Preferably, the electrochemical cell is adapted to be used

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with the apparatus in accordance with the first aspect of the
invention.

In accordance with a third aspect of the present invention, a
coupling device for electrically coupling a conductor to an
electrode for an electric chemical cell comprises a first
conducting member; a second conducting member, electrically
coupled and movably coupled to the first conducting member;
and a biasing device to bias the first and the second member
away from each other; the first conducting member being
adapted to be coupled to an electrical conductor and the
second member having an engagement portion adapted to engage
with and electrically couple the second member an electrode
for an electrochemical cell.

Preferably, one of the first and the second members is
slidably located within the other of the first and the second
members such that the engagement portion of the second portion
is biassed away from the first member by the biasing device.
Typically, the second member is slidably located within the
first member.

Preferably, the engagement surface of the second member is of
a material which provides a low electrical contact resistance
with the material of the electrode with which the engagement
surface is to be engaged. For example, the material of the
engagement portion may be a material which is harder than the
material of the electrode, such as titanium or iridium, or a

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material which has a low susceptibility to oxidation, such as
gold.

Typically, the first member may include an aperture in the
first member adapted to receive a generally cylindrical
electrically conducting member such that the conducting member
when inserted into the aperture is electrically coupled to the
first member.

An example of apparatus for voltammetric analysis in
accordance with the invention will now be described with
reference to the accompanying drawings, in which:-

    Figure 1 is a schematic diagram of apparatus for
    voltammetric analysis;
    Figure 2 is a side view of an electrochemical cell for
    use in the apparatus of Figure 1;
    Figure 3 is a cross-sectional view of an upper portion of
    the electrochemical cell shown in Figure 2;
    Figure 4 is a front view of the upper portion shown in
    Figure 3;
    Figure 5 is a cross-sectional view of an electrode for
    use in the cell shown in Figures 2 to 4;
    Figure 6 shows the apparatus of Figure 1 incorporated
    into a handheld voltammetric analyser;
    Figure 7 shows the apparatus of Figure 1 incorporated
    into an on-line voltammetric analyser;
    Figure 8 is a flow diagram illustrating the operation of

a diagnostic program for use with the apparatus shown in

Figures 1, 6 and 7; and,

Figure 9 is a graph showing calibration results and test

results obtained using the analyser shown in Figure 6.

Figure 1 is a block diagram of voltammetric analysis apparatus

1 which includes a microprocessor 2, an electrically erasable

programmable read only memory (EEPROM) 3, a display device 4

such as a liquid crystal display device, a memory device 5

which may be a random access memory (RAM), an interface device

6 such as an RS 232, a potentiostat 7, a cell controller 8, a

signal processor 9, and an input device, such as a keypad 10.

The cell controller 8 is adapted to be coupled to an

electrochemical cell 11 which is generally in the form of a

container with electrodes 14, 15, 16 and a stirrer 17.   An

example of an electrochemical cell 11 suitable for use with

the apparatus shown in Figure 1 is shown in more detail in

Figures 2 to 4.

The interface device 6 permits the apparatus 1 to be linked to

a computer, for example, to permit programming of the EEPROM 3

or to permit downloading of the memory 5 to a more permanent

storage device in the form of for example, magnetic media such

as a magnetic disk or tape.

The potentiostat 7 is coupled to the microprocessor 2 and

generates a scanning potential which is modified with various

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waveforms such as DC, AC, square wave or differential pulse,
in accordance with a chosen program downloaded from the EEPROM
3 to the microprocessor 2.

The cell controller 8 is coupled to the microprocessor 2 and
contains a group of switches. According to the chosen program
it will switch on or off the electrochemical cell 11 to allow
potential generated by the potentiostat 7 to be applied to the
electrodes 14, 15, 16 and to allow signals detected by the
electrodes 14, 15, 16 to be received by the signal processor
9. It also turns on and off the stirrer 17.

The signal processor 9 is coupled to the microprocessor 2. In
accordance with the chosen program it will receive signals
from the cell 11, process the signals, convert them into
digital information, and pass them to the microprocessor 2 to
be stored by the microprocessor 2 in the memory 5.

As shown in Figure 2, the electrochemical cell 11 includes a
container comprising a vessel 12 and an electrode holder 13 in
the form of a lid for the vessel 12. The lid 13 supports a
working electrode 14, a reference electrode 15 and a counter
electrode 16 as well as the stirring device 17. The stirring
device 17 comprises an electric motor 18 mounted on top of the
lid 13, a drive shaft 19 extending through the lid 13 into the
vessel 12 and a rotor 20 located at the end of the drive shaft
19 and adjacent to lower ends of the electrodes 14, 15, 16.

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Typically, the stirrer 17 is a 0.1W stirrer and the vessel 12

is a glass bottle with a volume of approximately 20ml. The

working electrode 14 may be a 3mm diameter disc glassy carbon

electrode, the counter electrode 16 may be a 3mm x 3mm

platinum electrode and the reference electrode 15 may be a

Ag/AgCl electrode.

The reference electrode 15 has a conventional reference

electrode construction. A cross-sectional view of the

electrode construction for the working and counter electrodes

14, 16 is shown in Figure 5. As shown in Figure 5, each of

the electrodes 14, 16 comprise an electrode sensing material

50 held in an electrode body 51. In the electrodes 14, 16 the

sensing material 50 is glassy carbon and platinum,

respectively. The body 51 encloses a coupling device which

comprises an outer casing 52, a contact pin 53 slidably

mounted within the casing 52 and a biassing device 54 within

the casing 52. The biassing device 54 acts to bias the pin 53

to an extended position in which a contact point 55 of the pin

53 is biassed against the sensing material 50 to make

electrical contact with the sensing material 50. The pin 53,

biassing device 54 and casing 52 are all electrically

conducting and the end of the casing 52, opposite to the end

from which the pin 53 extends, is electrically coupled to a

wire 56 which couples the sensing material 50 to the

controller 8.

In order to ensure a good electrical contact between the

contact point 55 and the sensing material 50, the pin 53, or

at least the contact point 55, is formed from a material which

is harder than the sensing material 50. This helps ensure a

good electrical contact as the contact point 55 "bites" into

the sensing material 50. For example, the pin 53 could be

manufactured from titanium or iridium.

The lid 13 of the cell 11 is shown in more detail in Figure 3

which shows a cross-sectional view of the lid 13 and Figure 4

which shows a top view of the lid 13. The lid includes a

central through bore 21 through which the drive shaft 19

extends and four side through bores 22, 23, 24, 25. The

working electrode 14 extends through the bore 23, the

reference electrode 15 extends through the bore 24 and the

counter electrode 16 extends through the bore 25. The bore 22

is left empty and may be used for introduction of analyte

and/or electrolyte into the vessel 12.

Due to the relative simplicity of the apparatus 1, the

apparatus can be incorporated into a relatively small handheld

analyser 30 as shown in Figure 6. The typical dimensions of

the handheld analyser 30 are 40mm x 100mm x 200mm and the

overall weight is typically approximately 0.5kg.

The handheld voltammetric analyser 30 incorporates the

apparatus shown in Figure 1 with the exception of the

electrochemical cell 11. In particular, the handheld

voltammetric analyser 30 includes the LCD display 4, the

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keypad 10, the communication interface 6 and a port 31 which permits the analyser 30 be connected to an external power supply.

However, as an alternative to, or in addition to, the external power supply, the handheld analyser 30 may be powered by an internal battery, such as any form of suitable conventional rechargeable battery. Typically, the battery may be recharged by the external power supply via the port 31 when necessary.

The remainder of the components, including the microprocessor 2, the EEPROM 3, the RAM 5, the potentiostat 7, the cell controller 8 and the signal processor 9 are contained within the housing of the analyser 30.

The handheld analyser 30 also has a communication port 33 which is coupled to the electrochemical cell 11 in use and is coupled internally to the cell controller 8. This permits the cell controller 8 to control the scanning voltage applied to the electrochemical cell and to receive the output signals from the electrochemical cell in response to the applied scanning voltage. In addition, the handheld analyser 30 may optionally be connected through the interface 6 to a remote computer, for example, to transfer data to the remote computer and/or to be remotely controlled by the remote computer.

In addition, the apparatus shown in Figure 1 can be incorporated into an on-line voltammetric analyser 60 as shown

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in Figure 7. The on-line analyser 60 is coupled via the

interface 6, local controller 34 and interface 35, to a remote

computer 36 which is used to remotely control the analyser 60.

The analyser 60 and the local controller 34 are powered by a

power supply 32 which may be battery operated or powered by a

mains power supply 37. In the analyser 60, the key board 10

is omitted, as instructions may be entered into the analyser

60 via the remote computer 36. However, apart from the

omission of the key board 10, the analyser 60 is identical to

the handheld analyser 30, described above and shown in Figure

6. The on-line analyser 60 is coupled via cable 61 and

connection port 33 to the electrochemical cell 11 and to

metering pumps 62, 63, 64, 65, 66 which can be operated to

pump liquid from reagent reservoirs 67, 68, 69, a sampling

valve 70 and a rinsing water valve 71, respectively into the

electrochemical cell 11. In addition, a vent valve 72 in the

electrochemical cell 11 can also be controlled by the remote

computer 36 or by local controller 34.

The liquid containing the sample to be analysed is connected

to the sampling valve 70, clean water is connected to the

rinsing valve 71 and standard reagents are stored in the

reagent reservoirs 67, 68, 69. The vent valve 72 is used to

empty the electrochemical cell 11 of liquid.

In use, the handheld analyser 30 and the on-line analyser 60

are set up by programming into the EEPROM 3 digital

information corresponding to the configuration of the

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electrochemical cell 11 to be used with the analyser 30, 60.

Such information includes details of the working electrode,

reference electrode, stirrer and vessel. For example, typical

information may be that the cell contains a 3mm diameter disc

glassy carbon electrode, a 3mm by 3mm platinum counter

electrode, a Ag/AgCl reference electrode, a 0.1W stirrer, a

20ml vessel and an electrode holder to fix each electrode

position.

The second step is to formulate a reagent with a known

composition as a testing media and convert it into digital

information. The formulated reagent will contain a standard

analyte, a buffer, a masking agent, a supporting electrolyte,

a preservative and a performance enhancer. The standard

analyte with known concentration is used to calibrate the cell

11. The concentration range is typically from 1ppb to

1000ppm. The buffer is used to control pH and usually

contains a salt and an acid or a base. The masking agent is

used to reduce interference from samples, which may be a

complex agent, an organic solvent, a precipitation agent, a

redox agent, a salt, etc. The supporting electrolyte is an

ionic compound to provide conductivity. The preservative

prolongs shelf life of the reagent. The performance enhancer

can increase selectivity and sensitivity of the reagent.

A voltammetric analysis is then performed under fixed

experimental conditions such as scan waveform, initial

potential, scan rate, final potential, current range, etc.

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This arrangement makes a voltammetric response position
(potential) easily identifiable. The conditions can be
obtained according to published papers, previous experience
and expert knowledge. All data is converted into digital
information.

Voltammetric response is searched for automatically by the
analyser 30, 60. The voltammetric response potential is
determined for the highest current reading in a certain time
period while voltammetric response current is calculated by
subtracting background current from current reading. This
procedure is programmed into the EEPROM 3.

System testing is then performed using the standard reagent.
As cell configuration, testing media and experimental
conditions are fixed, voltammetric response to the analyte in
the testing media should be a constant. Any significant
changes of response potential or current will indicate system
errors such as reference electrode failure or working
electrode fouling. The purpose of the system testing step is
to find and display these errors by comparing measured values
with pre-set values. This procedure is programmed into the
EEPROM 3.

The electrodes are then calibrated automatically.
Voltammetric analysis of the standard reagent is carried out
in the testing media. The response potential and current is
stored. This procedure makes sure that the electrodes are

calibrated just before sample analysis so that the electrode
surface condition remains unchanged. This calibration
procedure is programmed into the EEPROM 3.

A test sample is then analysed. This is performed by
voltammetric analysis of a test sample by mixing a known
volume of the test sample with a known volume of the standard
reagent. The response potential and current is compared with
stored response for the standard reagent and the result is
calculated and reported. This procedure is also programmed
into the EEPROM 3.

The EEPROM 3 also includes a diagnostic program which is
illustrated schematically in the flow diagram shown in Figure
8. In particular, the diagnostic program checks 70 the
results of the analysis to ensure that a peak current is
detected in the voltammetric analysis. If the peak current is
not detected, the microprocessor displays 71 an error message
in the LCD 4 and stops 72 the analysis. The diagnostic
program also uses the reference potential value range stored
in the data in the EEPROM 3 and compares this with the peak
current response at maximum intensity to check 73 the
reference electrode status. If the reference potential value
is out of range, the analyser outputs 74 an error message to
the operator and stops 75 the analysis. The diagnostic
program also uses the reference current data in the EEPROM 3
and compares this with the maximum response intensity obtained
during analysis to check 76 gain and working electrode status.

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If the maximum response intensity detected is out of range of

the reference current data, the diagnostic program causes the

microprocessor to instruct the signal processor 9 to change 77

to a more suitable gain level and the analysis is continued.

If the diagnostic program detects that no gain is available,

the microprocessor outputs 78 an error message to the operator

and stops the analysis 79. This permits the diagnostic

program to optimise the signal collection potential range and

current range which is stored in the memory 5.

In addition, the diagnostic program uses the reference data

stored in the EEPROM 3 which is compared with the actual peak

current response obtained from the standard reagent to

determine whether the peak current obtained from standard

reagent corresponds to the peak current expected from the

standard reagent. In the event that the peak current obtained

is outside a certain deviation from the expected peak current,

the microprocessor will output an error or warning message to

the operator.

After programming of the EEPROM 3, the analyser 30, 60 can be

used in conjunction with the cell 11 to run a voltammetric

analysis on a particular analyte. Initially, an operator

turns on the analyser 30, 60 being used and enters the analyte

to be analysed and the concentration of interest. The

operator then formulates a standard reagent for the analyte of

interest and adds this to the electrochemical cell 11 through

the aperture 22.

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The analyser 30, 60 then conducts a test on the reagent to check the conditions of the system automatically.

After this test, electrode status and instrument readiness will be reported and some analysis conditions such as gain and peak position will be set automatically. Any system errors detected by the diagnostic program will stop analysis with correction instructions. This enhances the performance and reliability of the apparatus.

As soon as the instrument is ready, the system is calibrated automatically. During the calibration process, the system collects and processes raw data and stores a response which represents a known concentration of the analyte to be tested for in the memory.

After the calibration process, a fixed volume of the test sample is added into the cell 11 and mixed with a fixed volume of the standard reagent. The system then collects and processes the voltammetric raw data again. The response which represents the concentration of the standard plus the sample is stored in the memory. The microprocessor 2 performs a calculation to determine the concentration of the analyte in the test sample using the information from the calibration sample and the result will be reported and displayed.

An example of use of the analyser 30 and cell 11 to analyse the concentration of Cu^{2+} in a waste water sample will now be

described. However, the analyser 60 could be used in the same

manner to perform the analysis.

A standard reagent containing 2 ppm copper nitrate, 0.5 M

acetic acid, 0.5 M sodium acetate and 20 ppm mercury chloride

was prepared. The formulation of the reagent was digitally

coded and entered into the EEPROM 3. In addition, a linear

anodic stripping voltammetry scan was also programmed into the

EEPROM 3 with the following conditions:

    (i)   An initial potential of -0.8V;

    (ii)   Pre-electrolysis for 30s;

    (iii)   A scan rate of $100mVs^{-1}$;

    (iv)   A final potential of +0.5V; and

    (v)   An electrode cleaning time of 20s at +0.5V.

10ml of the reagent was then introduced into the vessel 12

through the aperture 22 as a standard and the voltammetric

analysis process was started using the keypad 10. When

started the microprocessor 2 prompts a user via the display 4

to enter the analyte to be tested for. The operator in

response to this enters "copper". The microprocessor 2 then

prompts a user via display 4 for the concentration of interest

and the user enters "1ppm" using the keypad 10. In response

to this information, the microprocessor 2 selects the

appropriate program stored in the EEPROM 3 for an analyte of

copper with a concentration of interest of 1ppm and this is

downloaded from the EEPROM into the microprocessor 2. The

microprocessor 2 then runs the chosen program and in response

to the program the microprocessor 2 generates control signals

to control the output from the potentiostat 7 to the cell

controller 8 and the signal processor 9 and the cell

controller 8 directly. By causing the cell controller 8 to

apply the pre-programmed linear anodic stripping voltammetric

conditions (i) to (v) listed above which form part of the

program downloaded from the EEPROM 3 into the microprocessor

2. Using the output signals from the reference and counter

electrodes 15, 16 which are temporarily stored by the

microprocessor 2 in the RAM 5, the microprocessor 2 then

analyses the test results and stores the results as a

calibration.

After the calibration is completed, the microprocessor 2

prompts a user via the display 4 to add the actual test

sample. At this point, the user replaces the 10ml of the

standard calibration reagent with 5ml of the calibration

reagent and 5ml of the waste water sample to be analysed. The

operator then informs the analyser 30 using the keypad 10 that

the cell 11 contains the sample to be tested and the analyser

repeats the linear anodic stripping voltammetry scan under the

same conditions as that conducted for the standard calibration

sample.

The microprocessor 2 then compares the results of the test

sample with the calibration sample and outputs the

concentration of Cu^{2+} found in the test sample by means of the

display 4.

In addition, an operator can subsequently or simultaneously download the results to the computer 36 for permanent storage and/or for graphical display and/or printing of the results.

A typical graphical display obtained from the analyser 30 is shown in Figure 9 for the above example. The graph shows the applied voltage versus the sensed current for the calibration sample (A) containing 1ppm Cu^{2+} ions and the waste water sample (B). It can be seen from the graph that sample B has a peak which is approximately 1.5 times greater than the calibration sample A indicating that the concentration of Cu^{2+} ions in the waste water sample B is approximately 2.2ppm. It should be noted that the same graphical display would be obtained using the analyser 60 for the analysis instead of the analyser 30.

In addition to copper, the apparatus 1 and electrochemical cell 11 can be used to detect concentrations of most ions. Examples of typical ions that can be detected are ions of titanium, vanadium, chromium, manganese, iron, cobalt, nickel, zinc, gallium, germanium, arsenic, silver, cadmium, indium, tin, antimony, tungsten, platinum, gold, mercury, thallium, lead and bismuth, as well as organic compounds such as aromatics, aldehydes, alcohols, ketones, ethers, quinones, halides, heterocyclics, nitrocompounds, amines, phenols, organic acids and organic metallics.

In fact the apparatus 1 and the cell 11 can be used to detect any ion which can be detected using conventional voltammetry.

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Concentrations that can be detected can be any concentration
which can be detected using conventional voltammetric
analysis, and typically any concentration in the range from
approximately 1ppb to 1000ppm.

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Claims

1. Apparatus for voltammetric analysis comprising a
processor; a first memory device coupled to the processor, the
first memory device comprising a programmable read only memory
and storing a number of electrochemical cell control programs;
an output device coupled to the processor; an input device
coupled to the processor; a second memory device coupled to
the processor; an electrochemical cell controller coupled to
the processor, the cell controller being adapted to be coupled
to an electrochemical cell; the processor device, in response
to an analyte input signal entered via the input device,
retrieving a corresponding electrochemical cell control
program, and instructing the cell controller to apply a
scanning voltage to an electrochemical cell coupled to the
cell controller in use, in accordance with the retrieved
control program, and processing output signals received by the
cell controller from the electrochemical cell, in response to
the applied scanning voltage, to obtain an indication of the
concentration of an analyte, corresponding to the analyte
input signal, in the electrochemical cell, and outputting the
indication to the output device.

2. Apparatus according to claim 1, wherein the programmable
read only memory is an electrically erasable programmable read
only memory.

3. Apparatus according to claim 1 or claim 2, wherein the

output device comprises a display device.

4. Apparatus according to any of the preceding claims, wherein the output device comprises an interface device which permits the processor to communicate with another processing device.

5. Apparatus according to any of the preceding claims, wherein the cell controller further comprises a potentiostat and a signal processor.

6. Apparatus according to any of the preceding claims, wherein the apparatus is for stripping voltammetric analysis.

7. An electrochemical cell comprises a container comprising a bottom portion, an upper portion and an opening to permit a liquid to be analysed to be introduced into the container; a stirring device depending from the upper portion into the bottom portion of the container; and a counter electrode and a working electrode depending from the upper portion into the bottom portion of the container.

8. An electrochemical cell according to claim 7, wherein the axis of rotation of the stirring device is substantially co-axial with the central vertical axis of the container and the counter and working electrodes are arranged around the stirring device.

26

9.   An electrochemical cell according to claim 7 or claim 8, wherein the upper portion of the container is disengageable from the bottom portion of the container.

10. An electrochemical cell according to any of claims 7 to 9, wherein the bottom portion forms a liquid containing device and the upper portion forms a lid for the bottom portion.

11. An electrochemical cell according to any of claims 7 to 10, further comprising a reference electrode depending from the upper portion of the container such that the reference electrode is adjacent the stirring device and located between the counter and the working electrodes.

12. Apparatus according to any of claims 1 to 6, and further comprising an electrochemical cell in accordance with any of claims 7 to 11.

13. A coupling device for electrically coupling a conductor to an electrode for an electric chemical cell comprises a first conducting member; a second conducting member, electrically coupled and movably coupled to the first conducting member; and a biasing device to bias the first and the second member away from each other; the first conducting member being adapted to be coupled to an electrical conductor and the second member having an engagement portion adapted to engage with and electrically couple the second member an electrode for an electrochemical cell.

14. A coupling device according to claim 13, wherein one of the first and the second members is slidably located within the other of the first and the second members such that the engagement portion of the second portion is biassed away from the first member by the biasing device.

15. A coupling device according to claim 14, wherein the second member is slidably located within the first member.

16. A coupling device according to any of claims 13 to 15, wherein the engagement surface of the second member is of a harder material than the material of electrode with which the engagement surface is to be engaged.

17. A coupling device according to any of claims 13 to 16, wherein, the first member includes an aperture adapted to receive a generally cylindrical electrically conducting member such that the conducting member when inserted into the aperture is electrically coupled to the first member.
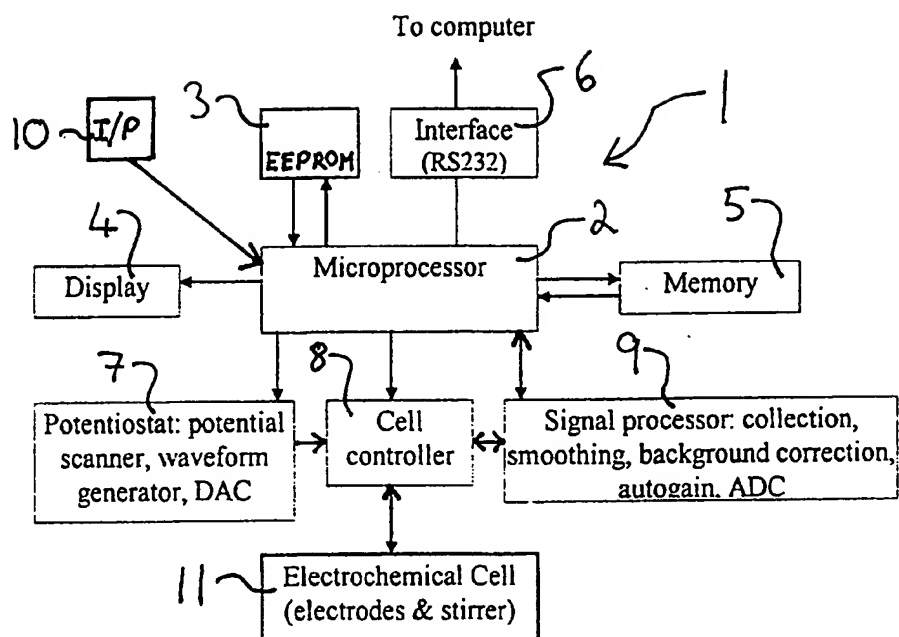
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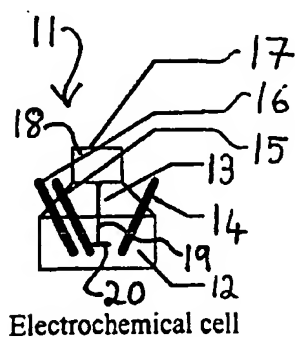

Figure 1

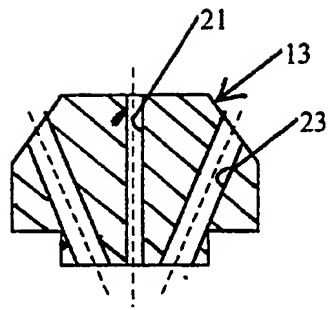

Electrochemical cell

Figure 2

Figure 3

Figure 4

Pole to the analyser

56

Electrode body

54

Spring of the contact

Shell of the contact

51   *52*

Hard pin of the contact

53

Sensor to the solution

55

50

Figure 5

Interface   6   To Computer   Connection port

External power supply

31   To cell

Display   33

                                                      4

                                                      30

Input   10

Figure 6

Power   6   61

Power Supply
32   31   33   11   Electrochemical Cell

37   Metering
                         4   63   Pumps

Local   62   64   65   66
Controller   60
34   71
                                              Vent   72
35   Interface   67   69   Valve   Sampling   Rinsing
                                                      70 Valve   Water Valve
                         68
Remote   Reagent Reservoirs
Computer
36
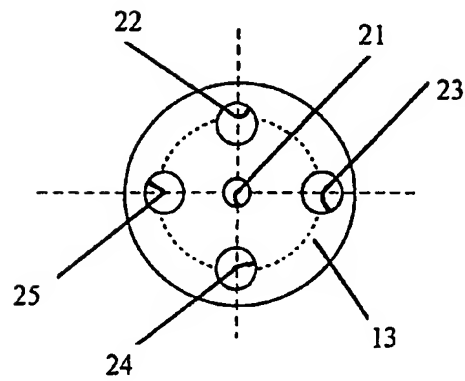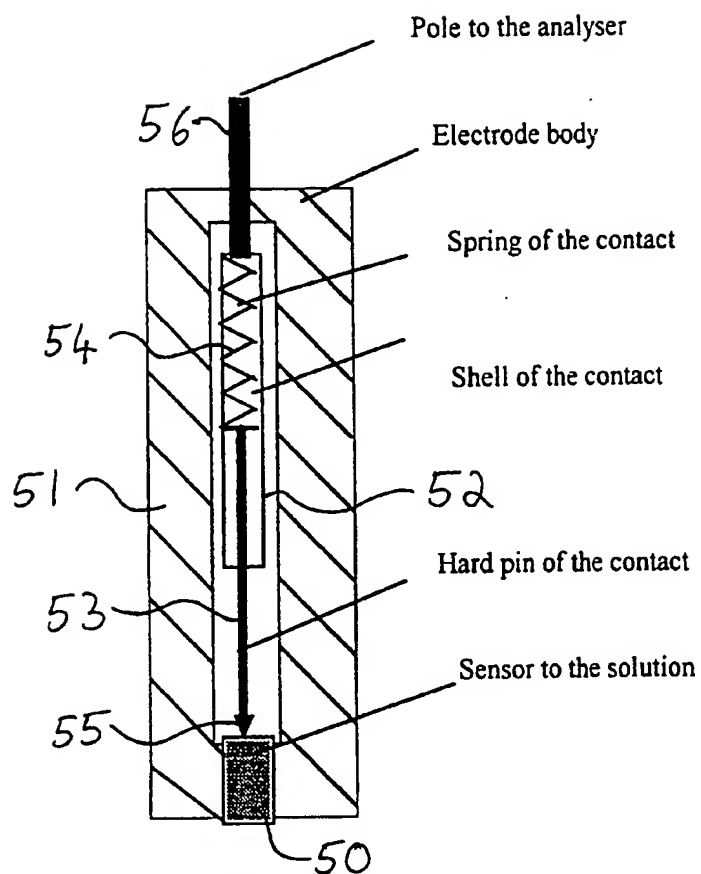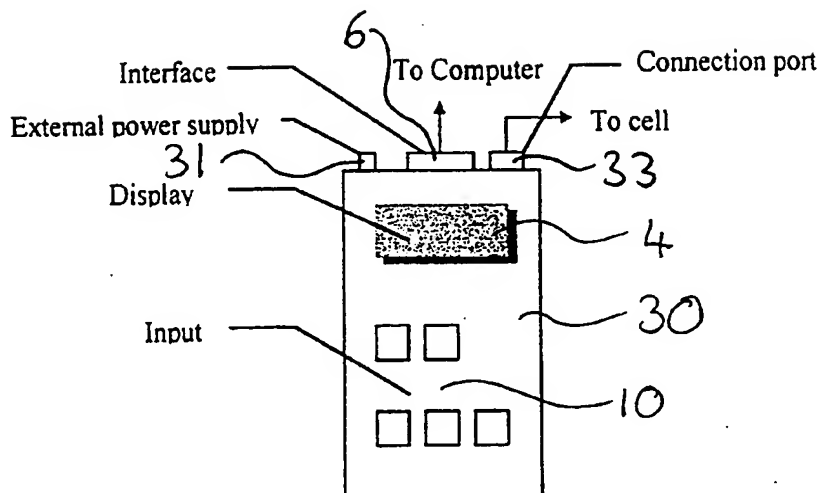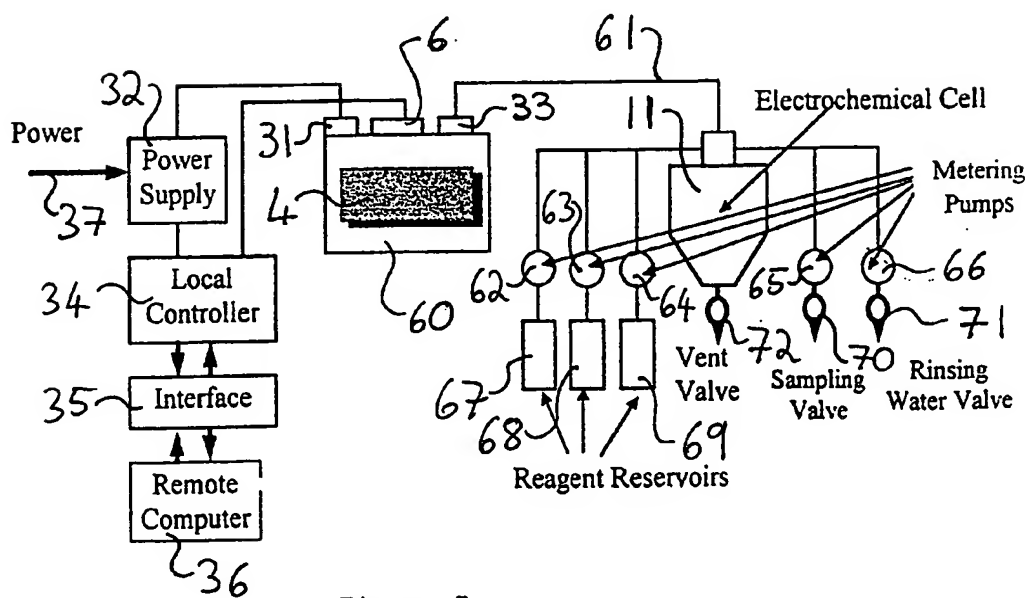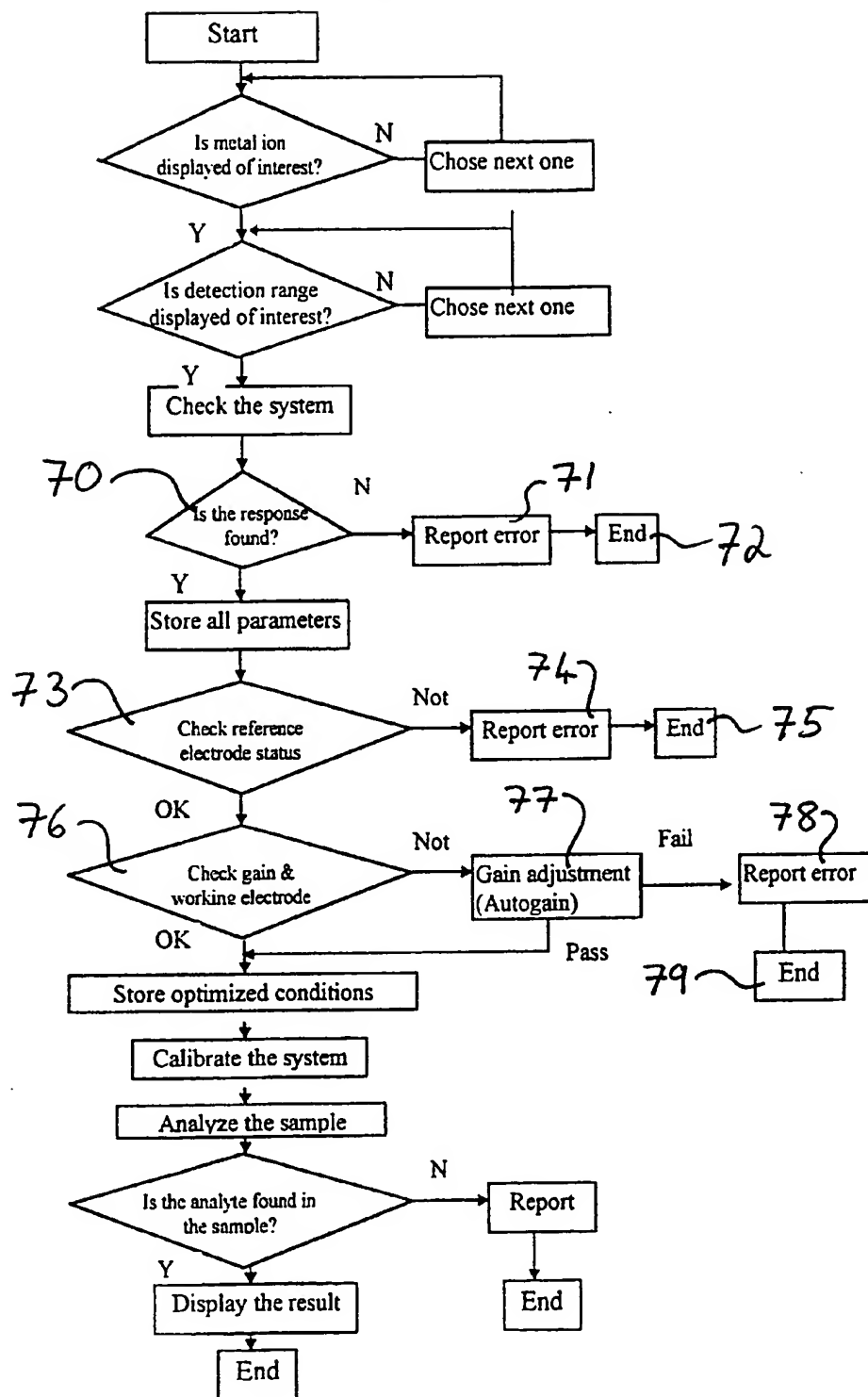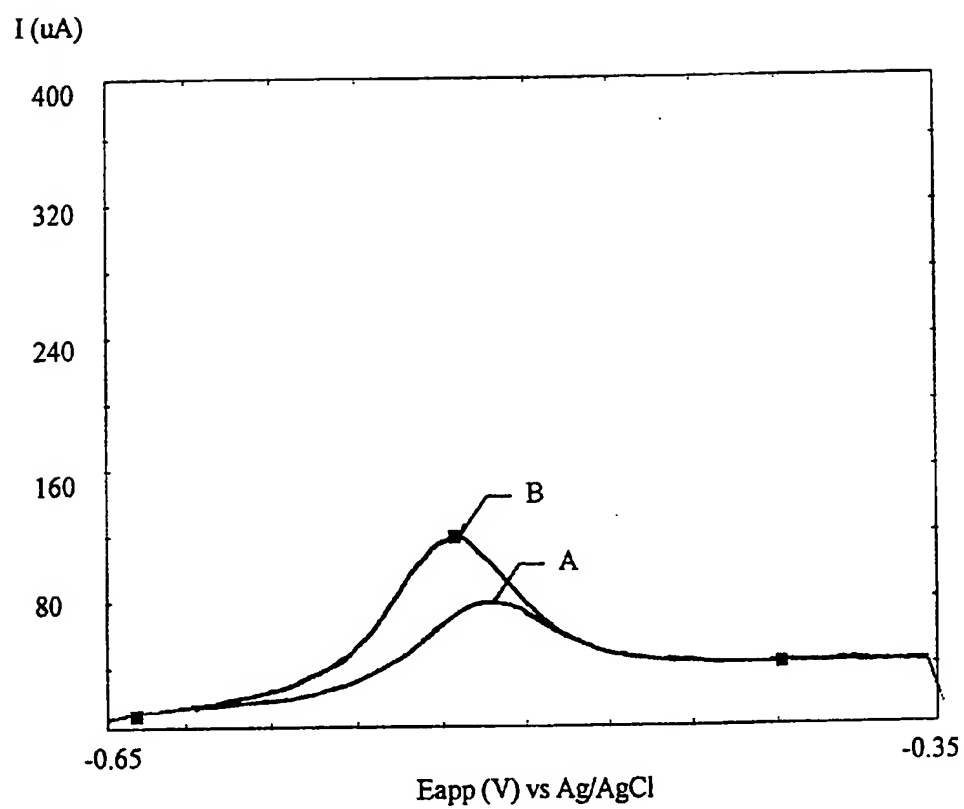
Figure 7

Figure 8

Figure 9

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC[7]: G 01 N 27/416

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC[7]: G 01 N 27/416

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98/36270 A2 (CHAMPAGNE), 20 August 1998 (20.08.98).	1
A	DE 2336402 A1 (CENTRALEC), 06 February 1975 (06.02.75).	7
A	RU 2069360 C1 (IVA CO LTD.), 20 November 1996 (20.11.96), Russian Patent Abstracts, Section S-X, week 9728, London: Derwent Publications Ltd., Class S03, AN 1997-256172.	13

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents:
„A" document defining the general state of the art which is not considered to be of particular relevance
„E" earlier application or patent but published on or after the international filing date
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„O" document referring to an oral disclosure, use, exhibition or other means
„P" document published prior to the international filing date but later than the priority date claimed

„T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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„&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 January 2000 (19.01.00)	16 February 2000 (16.02.00)

Name and mailing adress of the ISA/AT	Authorized officer
Austrian Patent Office Kohlmarkt 8-10; A-1014 Vienna Facsimile No. 1/53424/200	Nardai Telephone No. 1/53424/347

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